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14. ABSTRACT

The Air Force will require aerospace vehicles and weapon systems with performance superior to those of any potential adversary. Conductive nano-reinforcements offer an excellent potential for further improvement of structural performance and lightening protection of polymer composites used in numerous Air Force systems. Success in the proposed research will lead to scalable, low-cost method of producing SWNT/polymer composites thereby overcoming current obstacle to high volume loading of nanoreinforcement due to processing problems. Moreover, the research will lay a foundation for broader technology for multifunctional composite structures.

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Program Title: **Molecular Design Of Multilayer Composites From Carbon Nanotubes**

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1. Brief Description of the program and Research Approach

Previous generation of single wall carbon nanotubes (SWNT) composites suffer from poor connectivity with, and non-uniform distribution within, a polymer matrix resulting in structural defects. These defects are responsible for the mechanical failures of SWNT-polymer composites and the lower-than-expected mechanical performance. A new processing approach, based on sequential layering of chemically-modified nanotubes and polyelectrolytes, also known as layer-by-layer assembly (LBL) can greatly diminish the phase segregation and make SWNT composite highly homogeneous. Recent results[1] indicate that the tensile strength of these materials is several times higher than that of SWNT composites made via mixing; it approaches values typical for hard ceramics but the material itself is significantly lighter, which makes it one of the promising candidates for aviation applications especially for unmanned aerial vehicles (UAVs).

2. Major Goals and Objectives.

Our goal is to produce material with record properties using novel methods of SWNT orientation control and on-line assessment of mechanical properties of the composites. In addition to high structural uniformity provided by LBL, strengthening of bonding between graphene sheet and polymer matrix is be achieved through optimization of chemical interactions of SWNT with surrounding polymer. As well, it was proposed that the orientation of the individual SWNT fibers by magnetic field will result in significant improvement of strength. Unlike any other preparation methods, LBL makes possible production of highly nano- and micro-scale optimized materials from SWNTs.

These composites are expected to have unique mechanical properties with order-of-magnitude performance improvements.

3. Significant Accomplishments

1. The fundamental problem with formation of SWNT composites with high loading (70%), nanoscale uniformity, and complete exfoliation of SWNTs was resolved. No surfactants or wetting agents destroying interfacial transfer stress transfer were applied.

2. The record composites were made from SWNT stabilized by poly(styrenesulfonate) coupled with poly(vinylalcohol) by optimization of preparation conditions. The strengths obtained exceed **650 MPa**, which is an absolute record for *non-fibrous* SWNT composites. The Young's modulus exceeded **50 GPa**.

3. Mapping of the mechanical properties in respect to the

(a) oxidation state of SWNTs

(b) cross-linking modality;

(c) SWNT loading

was carried out (Table 1). Optimum position is likely located between 55 and 70% of SWNT loading.

4. The scale-up issues were addressed n this stage of the proposal. We developed several approaches that will enable large scale and 5-30 times faster manufacturing of the LBL composites than traditional LBL: (1) dewetting method and (2) exponential growth LBL; (3) spin-assisted LBL; and (4) Large scale LBL deposition (Figure 1).

Figure 1. Large scale LBL deposition system, "The Big Dipper".

5. Method of consolidation of the LBL films in the hierarchical composites was developed (Figure 2). We observed **strengthening** of the composites as the total volume increases as opposed to decrease of the strength according to the classical σ^2A=const expression. This is one of the first actual examples of **hierarchical composites**.

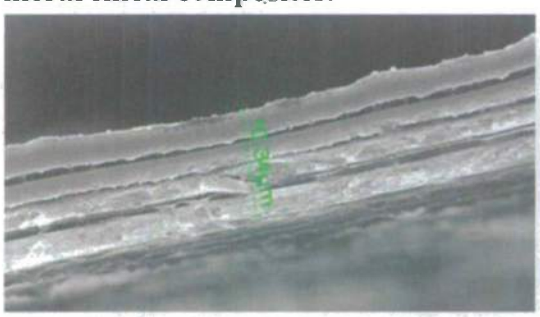

Figure 2. Consolidated LBL films.

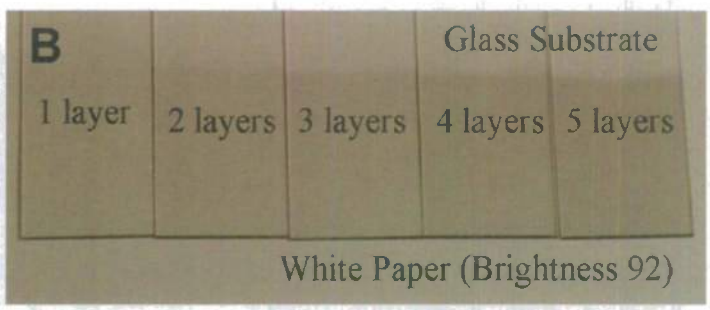

Figure 3. Conductive glass from SWNTs

6. We continued improving the conductivity of the LBL films of SWNT. The new method of detection of the damage in the airframe had been developed. New wireless sensors had been developed. Conductivity as high as $5*10^4$ S/cm was obtained. The best surface conduction was 80 Ohm per square for 80% transparency. Method of preparation of conductive glass from SWNT with tough flexible coating was found.

7. The same methods of LBL assembly developed for SWNT were applied to clays. The strongest clay composite with σ=450 MPa and Y=106 GPa was obtained. It was found that it has the ideal stress transfer even for high loadings, which is a critical fundamental discovery.

8. Method of improving fuel cell efficiency with free-standing LBL films was found.

Table 1 Comparison table of ultimate tensile strength (σ_{ult}), stiffness (E), toughness (K), strain (ε), and CNT loading for LBL composites and other materials.

Samples (estimated CNT loading)	Cross-linkage	σ_{ult} (MPa)	E (GPa)	K (J/g)	ε (%)
[PVA/SWNT$_{-COOH}$(15.8) +PSS] LBL (70%)	GA	391.5±36.8	13.2±2.4	42.8±10.5	18±4
	Heat	359.9±41.5	15.1±2.8	41.4±7.4	18±3
	-	257.2±24.6	11.9±2.5	13.8±3.8	11±1
PVA/SWNT$_{-COOH}$(7.9) +PSS] LBL (60%)	GA	504.5±67.3	15.6±3.8	121.2±19.2	39±3
	Heat	452.6±30.1	23.0±2.4	47.9±16.9	16±4
	-	224.5±15.1	11.6±2.0	26.9±10.5	19±7
[PVA/SWNT$_{-COOH}$(0) +PSS] LBL (47%)	GA	233.4±25.7	11.3±2.0	11.3±5.0	8±3
	Heat	262.57±2.1	10.9±0.8	12.8±1.5	8±1
	-	196.6±30.2	14.2±1.7	5.8±3.8	6±2
[PVA/Clay] LBL[6]	GA	400±40	106±11	~ 0.5	0.3±0.04
PVA[6]	-	40±4	1.7±0.2	~ 7.7	35±4
High performance CNT fiber[36] (100%)	-	8800	357	121	~8
SWNT Nylon composite fiber[55] (0.5%)	-	109	0.79	146	350
Kevlar fiber[84]	-	3600	90	33	5
Spider silk[84]	-	1150±200	7.9±1.8	165±30	39
Aluminum alloy (7075-T6)	-	572	71.7	29	11

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Future Plans:
Preparation of large scale samples.
Manufacturing large scale samples.
Preparations parts for UAVs.

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References: *(List one or two relevant publications resulting from the AFOSR funded work. If the AFOSR funded effort is new, please list one or two relevant references from your earlier work.)*

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